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TITLE: A method of manufacturing a thermostructural composite material bowl, in particular for an installation that produces silicon single crystals.

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My name and post office address are as stated above:

That I am knowledgeable in the English Language and the French Language and that I believe the English translation of the specification, claims, and abstract relating to International Application PCT/FR00/03275 filed November 24, 2000 is a true and complete translation.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true, and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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Title of the invention

A METHOD OF MANUFACTURING A THERMOSTRUCTURAL COMPOSITE MATERIAL BOWL, IN PARTICULAR FOR AN INSTALLATION THAT PRODUCES SILICON SINGLE CRYSTALS.

Field of the invention

The invention relates to thermostructural composite material bowls. A field of application of the invention is more particularly manufacturing bowls for receiving crucibles containing molten metal, such as silicon.

The term "thermostructural composite material" is used to mean a material comprising fiber reinforcement made of refractory fibers, e.g. carbon fibers or ceramic fibers, and densified by a refractory matrix, e.g. of carbon or of ceramics. Carbon/carbon (C/C) composite materials and ceramic matrix composite (CMC) materials are examples of thermostructural composite materials.

Background of the invention

A well-known method of producing silicon single crystals in particular for manufacturing semiconductor products consists in melting silicon in a crucible, in putting a crystal germ having a desired crystal arrangement into contact with the bath of liquid silicon, so as to initiate solidification of the silicon contained in the crucible with the desired crystal arrangement, and in mechanically withdrawing an ingot of single crystal silicon obtained in this way from the crucible. This method is known as the Czochralski method or as the "CZ" method.

The crucible containing the molten silicon is usually made of quartz (SiO_2). The crucible is placed in a bowl which is generally made of graphite, it being understood that proposals have also been made to make the bowl at least in part out of C/C composite materials. The bottom of the bowl stands on a support. For this purpose, the bottom of the bowl must be machined, in

particular so as to form a bearing surface for centering purposes and also a support zone. In addition, in the application in question, very high purity requirements make it necessary to use raw materials that are pure, with methods that do not pollute them, and with methods of purification in the finished state or in an intermediate state of bowl manufacture. For carbon-containing materials (such as graphite or C/C composites), methods of purification by high temperature treatment (at more than 2000°C) under an atmosphere that is inert or reactive (e.g. a halogen) are known and are commonly used.

The pieces of graphite used as bowls are fragile. They are often made up of as a plurality of portions (so-called "petal" architecture) and they cannot retain molten silicon in the event of the crucible leaking. This safety problem becomes more critical with the increasing size of the silicon ingots that are drawn, and thus with the increasing mass of the liquid silicon. Furthermore, graphite bowls are generally of short lifetime while being thick and thus bulky. It is preferable to use C/C composite material pieces which do not present those drawbacks and which, in particular, present better mechanical properties.

The manufacture of a C/C composite material piece, or more generally a piece of thermostructural composite material, usually comprises making a fiber preform having the same shape as the piece that is to be made, and that constitutes the fiber reinforcement of the composite material, and then densifying the preform with the matrix.

Techniques presently in use for making preforms include winding yarns by coiling yarns on a mandrel having a shape that corresponds to the shape of the preform that is to be made, draping which consists in superposing layers or plies of two-dimensional fiber fabric on a former matching the shape of the preform to

be made, the superposed plies optionally being bonded together by needling or by stitching, or indeed by three-dimensional weaving or knitting.

The preform can be densified in well-known manner using a liquid process or a gas process. Liquid process densification consists in impregnating the preform - or in pre-impregnating the yarns or plies making it up - with a matrix precursor, e.g. a carbon or ceramic precursor resin, and in transforming the precursor by heat treatment. Gas densification, known as chemical vapor infiltration, consists in placing the preform in an enclosure and in admitting a matrix-precursor gas into the enclosure. Conditions, in particular temperature and pressure conditions, are adjusted so as to enable the gas to diffuse into the core of the pores of the preform, so that on coming into contact with the fibers it forms a deposit of matrix-constituting material thereon by one of the components of the gas decomposing or by a reaction taking place between a plurality of components of the gas.

For pieces that are of relatively complex shape, for example bowl shaped, a particular difficulty lies in making a fiber preform having the right shape.

Another difficulty lies in obtaining densification in a manner that is reasonably simple and fast, in particular for bowls of large dimensions. Unfortunately, in the semiconductor industry, there exists a need for silicon ingots of ever greater diameter, thus requiring crucibles and support bowls to be provided that are of corresponding dimensions.

Object and summary of the invention

An object of the invention is to propose a method of manufacturing a bowl of thermostructural composite material that makes it possible to overcome the above difficulties, while remaining simple and low in cost.

According to the invention, the method comprises the steps which consist in:

· making a bowl preform by winding a yarn, the preform having an axial passage through its bottom;

· densifying the bowl preform by chemical vapor infiltration; and

· closing the passage by means of a plug.

Making a bowl preform with an axial passage presents two advantages. Firstly, the preform can be made by winding yarn without special difficulty. This would not be the case if a complete bowl preform had to be obtained by winding the yarn. In addition, while the preform is being densified by chemical vapor infiltration, the presence of an axial hole enhances flow of the gas and thus enhances densification.

A stiffened or consolidated bowl preform is preferably obtained prior to performing densification by chemical vapor infiltration. In conventional manner, a consolidated bowl preform is made by partial densification of a fiber structure having the desired shape, with the partial densification being at least sufficient to enable the preform to be handled. Partial densification can be performed by a gas process, or it can be performed by a liquid process, using impregnation by means of a precursor of the material that constitutes the matrix of the composite material, and transforming the precursor by heat treatment.

The perform can be consolidated by impregnation with a carbon precursor, e.g. selected from phenolic, furan, epoxy, and polyimide resins, and then transforming the precursor.

A consolidated preform is advantageously made by winding a yarn impregnated with said precursor.

Two consolidated preforms can be made simultaneously on a mandrel of a shape that corresponds to that of two facing bowl portions, with the yarn being wound over the

mandrel and with the resulting winding being cut in its middle portion.

Densifying the preform by chemical vapor infiltration makes it possible to obtain a carbon matrix having the continuity necessary to ensure that the installation for producing a silicon single crystal is not polluted with particles that come from the fibers or from resin coke formed on the fibers in order to consolidate the preform. A carbon matrix obtained by chemical vapor infiltration also presents better ability to withstand corrosion on coming into contact with a quartz crucible at high temperature.

Advantageously, the consolidated bowl preform is made from yarn that has no surface treatment, e.g. oxidation under controlled conditions using electrochemical or other means. In particular, the yarn can be a carbon yarn. The absence of the surface treatment which is usually provided on commercially-available yarns for providing surface functions that encourage bonding with organic matrices contributes to obtaining better dimensional stability by avoiding the appearance of internal stresses while making the composite material.

In another feature of the method, the method includes a step which consists in performing a final chemical vapor infiltration step after the passage has been closed by the plug, with the plug itself preferably being made of thermostructural composite material. The final infiltration step can include forming a matrix of a kind that is different from that formed previously during the steps of consolidating the bowl preform and the subsequent densification thereof. Thus, with a carbon densified preform, the final infiltration step can consist in depositing a ceramic matrix, e.g. of silicon carbide. Such an outer matrix material provides the composite material with protection against oxidation.

Advantageously, the bowl is subjected to high temperature purification and stabilization treatment, preferably at a temperature greater than 2200°C. Purification can be performed under an atmosphere of chlorine, as is well known for graphite. It makes it possible to remove impurities that might pollute the silicon when using the bowl as a support for crucibles containing silicon for manufacturing single crystal silicon ingots.

Such purification treatment can be performed on the consolidated bowl preform. The heat treatment then also contributes to avoiding dimensional variations during the subsequent manufacturing processes. Providing the plug closing the bottom of the bowl has also been subjected to purification treatment, performing purification after chemical vapor infiltration need not be necessary.

A protective coating can be formed at least on the inside of the bowl. Such a coating can be of pyrolytic carbon or "pyrocarbon", obtained by chemical vapor deposition, or it can be of ceramic, e.g. silicon carbide (SiC) likewise obtained by chemical vapor infiltration. In a variant, the inside face of the bowl can be provided with a protective layer, e.g. made of C/C composite material.

Brief description of the drawings

The invention will be better understood from the following detailed description given with reference to the accompanying drawings, in which:

· Figure 1 is a highly diagrammatic half-section view showing a bowl of composite material used as a crucible support in an installation for producing silicon ingots;

· Figure 2 is a flow chart showing the successive steps in a first implementation of a method in accordance with the invention; and

· Figures 3A to 3D are half-section views showing successive steps in making a bowl of composite material using the method of Figure 2.

Detailed description of implementations

As already mentioned, the field to which the invention applies is more particularly that of making bowls of thermostructural composite material for supporting crucibles in installations that produce single crystal silicon ingots.

Highly diagrammatic Figure 1 shows such a bowl of composite material, e.g. C/C composite material supporting a crucible 5 which is usually made of quartz. The bowl 1 stands on an annular support formed with a ring 2 mounted at the end of a shaft 3 having a setback 4 therein. The bowl has a bottom portion 1a and a surround portion 1b, part of which is substantially cylindrical and is connected to the bottom portion via a region of rounded profile. The bottom portion of the bowl 1 is machined so as to form a centering bearing surface corresponding to the setback 4 and a support surface on the ring 2.

After the crucible has been filled with silicon, the assembly is placed in a furnace and the temperature in the furnace is raised to a value which is high enough to cause the silicon to liquefy. At this temperature, the crucible softens and it matches the shape of the bowl. A germ having a desired crystal arrangement is then brought into contact with the bath of silicon and is extracted slowly therefrom, thereby forming a column between the germ and the bath. An ingot is thus drawn at very low speed, and its length can lie in the range 1 meter (m) to 2 m.

That method of manufacturing silicon ingots is well known and does not form part of the invention, such that a more detailed description is not required.

Because thermostructural composite materials have the ability to conserve good mechanical properties and good dimensional stability at high temperatures, they are particularly suitable for making bowls for use in the above application.

The description below relates more particularly to making bowls out of C/C composite materials with carbon fiber reinforcement and a carbon matrix, or at least a matrix that is essentially made of carbon. The invention also covers making bowls out of CMC type composite materials, i.e. having ceramic fiber reinforcement (e.g. made of SiC fibers) and a matrix that is also ceramic (e.g. likewise of SiC), where technologies for making CMCs are well known.

The fiber reinforcement is made from yarns of the kind commercially available but free from any of the surface treatment normally provided to provide surface functions that encourage bonding with an organic matrix when such yarns are used to form fiber/resin type composite materials that are not intended for high temperature applications. The absence of surface functions makes it possible to avoid internal stresses during the process of manufacturing the composite material using the method of the invention.

A first implementation of a method of manufacturing a bowl of composite material is described below with reference to Figures 2 and 3A to 3D.

A first step 10 of the method (Figure 2) consists in providing a mandrel 12 (Figure 3A). The shape of the mandrel corresponds to the shape of the two parts of the outlines of the bowls that are to be made placed rim-to-rim. At its axial ends, the mandrel is associated with rings 14 which leave an annular gap 16 formed in the outside surfaces thereof at the periphery.

By way of example, the mandrel 12 and the rings 14 can be made of metal. The assembly is mounted and prevented from moving axially on a shaft 18 which passes

through central passages of the rings 14 and is connected to a rotary drive motor (not shown).

A second step 20 in the method consists in winding a yarn onto the mandrel 12.

The winding 22 is made using a yarn that is pre-impregnated with a liquid precursor of carbon, e.g. a phenolic resin. At the axial ends of the mandrel, the winding extends far enough to be wound in part around the rings 14 in the vicinity of the recesses 16. Winding is continued so as to build up the thickness desired for the preforms that correspond to the bowl outline portions that are situated rim-to-rim (Figure 3B). The rings 14 make it easier to stop winding yarn at the axial ends of the winding. The rings 14 can be formed integrally with the mandrel 12. In order to avoid having excessive winding thickness in the vicinity of the end zones of the mandrel where diameter drops off quite quickly, winding can include a plurality of steps 24', 24", ..., at different diameters.

After winding, the blank 26 formed by the winding 22 and supported by the mandrel 12 is placed in an oven to polymerize the phenolic resin impregnating the yarn of the winding (step 30 of the method).

At the following step 40, the blank 26 is cut in half radially so as to obtain two half-shells 28 which are withdrawn from the mandrel 12 (Figure 3C), each half-shell having an axial passage 30.

Each half-shell 28 is then subjected to heat treatment (step 50) so as to carbonize the phenolic resin and obtain a consolidated bowl preform having an axial passage 30 through its bottom. The yarn winding is consolidated by being densified with a carbon matrix derived from transforming the phenolic resin. This provides a preform that is densified in part, i.e. that still presents accessible residual porosity, while nevertheless having sufficient strength to be handled.

Thereafter, the purified bowl preform is placed in an enclosure to be subjected to a step of densification by chemical vapor infiltration (step 60 of the method). Densification is performed to fill in, at least in part, the residual porosity in the consolidated preform with pyrolytic carbon. This is achieved in a manner that is well known in itself using a gas containing a hydrocarbon, such as methane or natural gas, constituting a precursor for the carbon.

A plurality of bowl preforms can be densified simultaneously within the same enclosure. To this end, the preforms are placed one above another, in axial alignment with gaps being left between them to allow the gas to flow. A method of chemical vapor infiltration with directed gas flow as described in US patent No. 5 904 957 can be used.

The step 60 of chemical vapor infiltration contributes not only to finishing off preform densification, but also to forming a continuous matrix of controlled microstructure that is capable of holding within the material any carbon particles from the fibers or grains of coke from the consolidating resin, such that there is no danger of these particles or grains giving rise to pollution when the bowl is in use. Compared with a carbon matrix as obtained using a liquid process, the carbon matrix obtained by chemical vapor infiltration also provides better resistance to corrosion on contact with a quartz crucible at high temperature.

The following step 70 of the method consists in machining the bottom portion of the bowl so as to fix a plug 34 that closes the passage 30 (Figure 3D). In the example shown, the plug 34 is made of two pieces 35 and 37, e.g. of C/C composite material (step 80) that have been subjected if necessary to a step of purifying the carbon. The piece 35 is saucer-shaped and its periphery forms a lip 35a that bears against the rim of the passage 30, on the inside of the bowl, while the piece 37 which

is also saucer-shaped has a rim 37a which bears against the rim of the passage 30 on the outside. The pieces 35 and 36 can be bonded together by screw fastening, with the piece 35 presenting a projecting central portion which is screwed into a housing in the piece 37. The pieces 35 and 37 clamp the rim 30a of the opening 30. The pieces 35 and 37 constituting the C/C composite material plug 34 can be made by any known method. For example, preforms can be made by superposing two-dimensional plies in the form of carbon fiber disks. The plies which can be woven cloth, for example, are bonded together by needling or by stitching. Thereafter they can be densified by means of a carbon matrix using a liquid process or by chemical vapor infiltration.

After the plug 34 has been installed (step 90) a new and final densification step 100 is performed using chemical vapor infiltration to provide final carbon matrix so as to ensure that the plug 34 is securely assembled to the bottom proton of the preform 28 and so as to finish off densification thereof. A C/C composite material bowl 36 is thus obtained ready for use, possibly after a final stage of machining to finish the bottom and plug portion 34.

The following step 110 of the method consists in purifying the carbon of the resulting bowl when the intended application requires the bowl to be free from impurities. This applies to installations for drawing a silicon single crystal for use in manufacturing semiconductor products, in which the silicon must initially be uncontaminated by any impurities. The carbon can be purified by heat treatment at a temperature that preferably lies in the range 2200°C to 3000°C, e.g. a temperature equal to about 2400°C, under a non-oxidizing atmosphere, e.g. under an atmosphere of chlorine, and at a pressure that is preferably less than 100 kiloPascals (kPa) for example is equal to about 10 kPa. Such heat treatment under chlorine is well known

in itself for purifying graphite. The heat treatment also serves to stabilize the dimensions of the consolidated bowl preform. In a variant, purification could be performed once the bowl preform has been consolidated, after step 50. Insofar as the plug 34 has also been subjected to purification, the final purification step after chemical vapor infiltration could then be omitted.

When the bowl is for receiving a quartz crucible, it can be desirable to protect the bowl from erosion caused by a chemical reaction between quartz (SiO_2) and the carbon of the bowl at the temperature at which the crucible is used. When drawing a single crystal of silicon, the crucible is raised to a temperature of about 1600°C at which quartz becomes soft, is subject to creep, and fits closely to the shape of the supporting bowl, while also tending to become reactive.

Protection can be obtained by forming a protective coating (step 120) at least on the inside of the bowl. The protective coating can be of pyrolytic carbon or "pyrocarbon" obtained by chemical vapor deposition, or it can be made of ceramic, e.g. silicon carbide (SiC) likewise obtained by chemical vapor infiltration. In a manner that is well known per se, an SiC deposit can be obtained by chemical vapor deposition using a gas that contains a precursor of SiC, such as methyltrichlorosilane (MTS).

The protective coating can be formed continuously running on from the final densification step 100, prior to any final heat treatment step for purification.

In a variant, the bowl can be protected by interposing an intermediate layer between the bowl and the crucible, said layer matching the shape of the bowl, e.g. being a protective layer of a thermostructural composite such as a C/C composite obtained by densifying a fiber preform constituted by a carbon felt or by two-dimensional plies of carbon fibers.

Figure 1 shows such a protective layer 6 lining the inside face of the bowl 1. This protective layer is consumable, and the bowl is re-lined periodically.

Although a description above relates to winding a blank suitable for making two bowl blanks simultaneously, the bowl blanks could naturally be made individually.